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*Catalytic Reduction of Carbon Dioxide by Metal Centers*

*Final Report*

by

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*Summary*

The results of the work carried out under this ONR contract include the following significant discoveries. (1) We have demonstrated the first homogeneous catalytic hydrogenation/reduction of carbon dioxide to the methyl group ( $-\text{CH}_3$ ,  $\text{C}^{2-}$ ) in the presence of several transition metal complexes (in previous work, the reduction has terminated at the  $\text{C}^{2+}$  level). (2) Another catalytic system has been found to reduce  $\text{CO}_2$  to elemental carbon via formamide intermediation. (3) A platinum cluster complex has been discovered which catalyzes the  $\text{CO}_2$  reduction reversibly under ambient conditions, both unusual in homogeneous catalysis by metal complexes. The same Pt compound is the most active homogeneous catalyst for  $\text{CO}_2$  hydrogenation reported to date. (4) Other significant developments include (a) the preparation of metallic catalysts (Cr, Mo, W, Re) and their use in  $\text{CO}_2$  reduction, and (b) the discovery of reversible  $\text{CO}_2$  activation by metal complexes monitored by FT-IR techniques *in situ*. All these advances have substantially contributed to our understanding of the factors which determine the catalytic reduction of carbon dioxide.

*Previously Submitted Reports and Publications*

*A. Technical Reports*

(1) Reversible Homogeneous Catalysis of Carbon Dioxide Hydrogenation/Reduction at Room Temperature and Low Pressures Mediated by a Platinum(0)-Diphosphine Cluster Complex in Solution, by S. Schreiner, J.Y. Yu, L. Vaska, 1987-07-22.

(2) Carbon Dioxide Reduction via Homogeneous Catalytic Synthesis and Hydrogenation of N,N-dimethylformamide, by S. Schreiner, J.Y. Yu, L. Vaska, 1988-02-25.

(3) Catalytic Activation of Carbon Dioxide by Metal Complexes, by L. Vaska, 1988-03-15.

(4) Homogeneous Catalytic Production of Hydrogen and Other Molecules from Water-DMF Solutions, by J.Y. Yu, S. Schreiner, L. Vaska, 1988-07-08.

(5) Catalytic Reduction of Carbon Dioxide to Methane and Other Species via Formamide Intermediation: Synthesis and Hydrogenation of  $\text{HC(O)NH}_2$  in the Presence of  $[\text{Ir}(\text{Cl})(\text{CO})(\text{Ph}_3\text{P})_2]$ , by L. Vaska, S. Schreiner, R.A. Felty, J.Y. Yu, 1988-10-13.

*B. Progress Report* included in the Renewal Proposal, "Catalytic Reduction of Carbon Dioxide by Metal Centers", pp. 4-10, by L. Vaska, 1988-06-30.

*C. Performance Report* on Fourier-Transform Infrared Spectrometer (FT-IR), by L. Vaska, 1987-11-18. This instrument was obtained with grant #N00014-87-G-009, "New Approaches to Catalysis by Metal Centers".

*D. End-of-the-Year Reports* by L. Vaska: 1985-09-26; 1986-09-23; 1987-07-11; 1989, to be submitted by June 1.

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*E. Conference Abstracts*

(1) Catalytic Activation of Carbon Dioxide by Metal Complexes, by L. Vaska; invited lecture at the conference on Chemical Physics of Enzyme Catalysis, Tallinn, Estonia, September 1987.

(2) Reversible Catalytic Reduction of Carbon Dioxide Mediated by Metal Complexes in Solution at Mild Conditions, by L. Vaska; paper presented at ONR/GRI Workshop on CO<sub>2</sub> Reactivity and Reduction, Menlo Park, CA, April 1988.

(3) Catalytic Reduction of Carbon Dioxide to Methane and Other Species via Formamide Intermediation, by L. Vaska; invited lecture to be given at the 19th Northeast Regional Meeting of the American Chemical Society, Albany, NY, June 1989.

(4) From CO<sub>2</sub>, NH<sub>3</sub> and H<sub>2</sub> to CH<sub>4</sub>, HCN, Ar-C<sub>3</sub>H<sub>3</sub>N<sub>3</sub> and Other Species via Catalytic Synthesis, Hydrogenation and Decomposition of Formamide, by L. Vaska; invited lecture to be given at the NATO-Advanced Study Institute, Summer School on Enzymatic and Model Carboxylation and Reduction Reactions for Carbon Dioxide Utilization, Ginos, Italy, June 1989.

(5) A Tertiary Phosphine-Metal Complex, [Ir(Cl)(CO)(Ph<sub>3</sub>P)<sub>2</sub>]: Discovery, Mechanism of Formation, and Catalytic Properties, by L. Vaska; invited lecture to be given at the 11th International Conference on Phosphorus Chemistry, Tallinn, Estonia, July 1989.

*F. Publications (see A. Technical Reports, numbers cited below)*

(1) S. Schreiner, J.Y. Yu, L. Vaska, *J. Chem. Soc., Chem. Commun.*, 602 (1988) (No. 1).

(2) S. Schreiner, J.Y. Yu, L. Vaska, *Inorg. Chim. Acta*, 147, 139 (1988) (No. 2).

(3) L. Vaska, *J. Mol. Catal.*, 47, 381 (1988) (No. 3).

(4) L. Vaska, S. Schreiner, R.A. Felty, J.Y. Yu, *J. Mol. Catal.*, in press (No. 5).

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